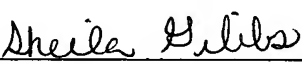


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<u>Sheila Gibbs</u>	
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## FLUID LOSS ADDITIVES FOR CEMENT SLURRIES

### Cross-Reference to Related Applications

[0001] This application is a continuation-in-part of prior Application No: 10/795,158 filed March 5, 2004, the entire disclosure of which is incorporated herein by reference, which is a continuation-in-part of prior Application No. 10/738,199 filed December 17, 2003, the entire disclosure of which is incorporated herein by reference, which is a continuation-in-part of prior Application No. 10/727,370 filed December 4, 2003, the entire disclosure of which is incorporated herein by reference, which is a continuation-in-part of prior Application No. 10/686,098 filed October 15, 2003, the entire disclosure of which is incorporated herein by reference, which is a continuation-in-part of prior Application No. 10/623,443 filed July 18, 2003, the entire disclosure of which is incorporated herein by reference, and which is a continuation-in-part of prior Application No. 10/315,415, filed December 10, 2002, the entire disclosure of which is incorporated herein by reference.

### Background

[0002] The present embodiment relates generally to methods and cement compositions for cementing in a subterranean zone, and more particularly, to cement fluid loss control additives, cement compositions containing the additives, and methods of using the cement compositions.

**[0003]** Hydraulic cement compositions are commonly utilized in subterranean well completion and remedial operations. For example, hydraulic cement compositions are used in primary cementing operations whereby strings of pipe such as casings and liners are cemented in well bores. In performing primary cementing, a hydraulic cement composition is pumped into the annular space between the walls of a well bore and the exterior surfaces of a pipe string disposed therein. The cement composition is permitted to set in the annular space, thereby forming an annular sheath of hardened substantially impermeable cement therein, which supports and positions the pipe string in the well bore and bonds the exterior surfaces of the pipe string to the walls of the well bore. Hydraulic cement compositions are also utilized in remedial cementing operations such as plugging highly permeable zones or fractures in well bores, plugging cracks or holes in pipe strings, and the like.

**[0004]** Fluid loss control agents are used in cement compositions to reduce fluid loss from the cement compositions to the permeable formations or zones into or through which the cement compositions are pumped.

#### **Description**

**[0005]** In carrying out certain methods disclosed herein, cementing is performed in a subterranean zone by placing a cement composition comprising a mixing fluid, zeolite, cementitious material, and proportioned fluid loss additives (FLAs) as described herein, into the subterranean zone and allowing the cement composition to set therein.

**[0006]** According to exemplary methods of sealing a wellbore, a cement composition is formed by mixing a cement mix, which includes a base blend and proportioned fluid loss additives (FLAs), with a mixing fluid. The cement composition is placed in the subterranean zone and allowed to set therein. The base blend used in such methods includes zeolite and at least one cementitious material, and the proportioned FLAs include at least a first fluid loss additive having a first molecular weight and at least one second fluid loss additive having a second molecular weight that is less than the first molecular weight. The first fluid loss additive will be hereafter referred to as the “high molecular weight FLA” and the second fluid loss additive will be hereafter referred to as the “low molecular weight FLA”.

[0007] According to certain methods disclosed herein, the proportionality of the FLAs can be described by a ratio. For example, the proportionality of the FLAs can be expressed as a ratio of the amounts of each FLA, where each amount is expressed as a weight percent of the total weight of the base blend (% bwob). Thus, in certain examples described herein, the proportionality of the FLAs can be described by a ratio of about 15:85, of a high molecular weight FLA to a low molecular weight FLA. In other examples, the amount of low molecular weight FLAs present in the base can be increased or decreased, with a complementary increase or decrease in the amount of high molecular weight FLAs. According to one such example, the amount of low molecular weight FLAs in the base blend decreases to about 0.75 % bwob, and the amount of high molecular weight FLAs increases to about 0.25 % bwob. In such an example, the proportionality of the FLAs can be described by a ratio of about 25:75 of high molecular weight FLAs to low molecular weight FLAs.

[0008] In another example, the proportionality of the FLAs can be expressed as a ratio of the amount of high molecular weight FLA(s) to the amount of low molecular weight FLA(s), irrespective of the amount each type contributes to the base blend. Thus, in certain examples described herein, the proportionality of the FLAs can be described as a ratio of about 1:5.67, meaning that the amount of low molecular weight FLAs present in the base blend is about 5.67 times the amount of high molecular weight FLAs present in the base blend. According to an example where the amount of low molecular weight FLAs present in the base blend has been decreased, such as to the 0.75 % bwob described above, and the amount of high molecular weight FLAs has been increased, such as to 0.25 % bwob described above, the proportionality of the FLAs can be described by a ratio of about 1:3 of high molecular weight FLAs to low molecular weight FLAs.

[0009] Yet another way to express the proportionality of the FLAs as a ratio is in terms of their molecular weights. According to certain methods, the high molecular weight FLA has a molecular weight in the range of from about 800,000 atomic mass units to about 1,200,000 atomic mass units, and the low molecular weight FLA has a molecular weight in the range of from about 100,000 atomic mass units to about 300,000 atomic mass units. Thus, in certain examples, the proportionality of the FLAs can be described as a ratio of about 12:1, meaning that

the molecular weight of the high molecular weight FLA would be about 12 times the molecular weight of the low molecular weight FLA. In other examples described herein, the proportionality is described as a ratio of about 4:1, meaning that the molecular weight of the high molecular weight FLA is about 4 times the molecular weight of the low molecular weight FLA. In still other examples, the proportionality of the FLAs can be described by a ratio of about 2.66:1, meaning that the molecular weight of the high molecular weight FLA would be about 2.66 times the molecular weight of the low molecular weight FLA

**[0010]** In carrying out other methods disclosed herein, a cement mix is prepared by forming a base blend comprising zeolite and at least one cementitious material, and mixing the base blend with proportioned fluid loss additives as described herein.

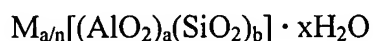
**[0011]** Thus, cement compositions and cement mixes as disclosed herein include proportioned fluid loss additives (FLAs). In certain exemplary compositions and mixes, the FLAs are non-ionic water based soluble polymers. According to other examples, the FLAs are hydrophobically modified non-ionic water based soluble polymers. In certain examples described herein, the FLAs are unmodified hydroxyethylcelluloses. In still other examples, the FLAs are hydrophobically modified hydroxyethylcelluloses.

**[0012]** Exemplary cement mixes include a base blend and proportioned fluid loss additives. The base blend includes zeolite and at least one cementitious material. The proportioned fluid loss additives are as described above, that is, at least one high molecular weight FLA and at least one low molecular weight FLA, and where the high molecular weight FLA and the low molecular weight FLA are present in the base blend in a ratio of about 1:5.67. According to certain examples, the high molecular weight FLA comprises a hydroxyethylcellulose having a molecular weight in the range of from about 800,000 atomic mass units to about 1,200,000 atomic mass units, and the low molecular weight FLA comprises a hydroxyethylcellulose having a molecular weight in the range of from about 100,000 atomic mass units to about 300,000 atomic mass units.

**[0013]** A variety of cementitious materials can be used in the present methods, mixes and compositions, including but not limited to hydraulic cements. Hydraulic cements set and harden by reaction with water, and are typically comprised of calcium, aluminum, silicon, oxygen,

and/or sulfur. Hydraulic cements include micronized cements, Portland cements, pozzolan cements, gypsum cements, aluminous cements, silica cements, and alkaline cements. According to preferred embodiments, the cementitious material comprises at least one API Portland cement. As used herein, the term API Portland cement means any cements of the type defined and described in API Specification 10, 5<sup>th</sup> Edition, July 1, 1990, of the American Petroleum Institute (the entire disclosure of which is hereby incorporated as if reproduced in its entirety), which includes Classes A, B, C, G, and H. According to certain embodiments disclosed herein, the cementitious material comprises Class C cement. Those of ordinary skill in the art will recognize that the preferred amount of cementitious material is dependent on the type of cementing operation to be performed.

**[0014]** Zeolites are porous alumino-silicate minerals that may be either a natural or manmade material. Manmade zeolites are based on the same type of structural cell as natural zeolites and are composed of aluminosilicate hydrates having the same basic formula as given below. It is understood that as used in this application, the term “zeolite” means and encompasses all natural and manmade forms of zeolites. All zeolites are composed of a three-dimensional framework of SiO<sub>4</sub> and AlO<sub>4</sub> in a tetrahedron, which creates a very high surface area. Cations and water molecules are entrained into the framework. Thus, all zeolites may be represented by the crystallographic unit cell formula:



where M represents one or more cations such as Na, K, Mg, Ca, Sr, Li or Ba for natural zeolites and NH<sub>4</sub>, CH<sub>3</sub>NH<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>NH, (CH<sub>3</sub>)<sub>4</sub>N, Ga, Ge and P for manmade zeolites; n represents the cation valence; the ratio of b:a is in a range of from greater than or equal to 1 to less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.

**[0015]** Preferred zeolites for use in the cement compositions prepared and used according to the present disclosure include analcime (hydrated sodium aluminum silicate), bikitaite (lithium aluminum silicate), brewsterite (hydrated strontium barium calcium aluminum silicate), chabazite (hydrated calcium aluminum silicate), clinoptilolite (hydrated sodium aluminum silicate), faujasite (hydrated sodium potassium calcium magnesium aluminum silicate),

harmotome (hydrated barium aluminum silicate), heulandite (hydrated sodium calcium aluminum silicate), laumontite (hydrated calcium aluminum silicate), mesolite (hydrated sodium calcium aluminum silicate), natrolite (hydrated sodium aluminum silicate), paulingite (hydrated potassium sodium calcium barium aluminum silicate), phillipsite (hydrated potassium sodium calcium aluminum silicate), scolecite (hydrated calcium aluminum silicate), stellerite (hydrated calcium aluminum silicate), stilbite (hydrated sodium calcium aluminum silicate) and thomsonite (hydrated sodium calcium aluminum silicate). In exemplary cement compositions prepared and used according to the present disclosure, the zeolite is selected from the group consisting of analcime, bikitaite, brewsterite, chabazite, clinoptilolite, faujasite, harmotome, heulandite, laumontite, mesolite, natrolite, paulingite, phillipsite, scolecite, stellerite, stilbite, and thomsonite. According to still other exemplary cement compositions described herein, the zeolite used in the cement compositions comprises clinoptilolite.

**[0016]** According to still other examples, in addition to proportioned fluid loss additives as described herein, the cement compositions, cement mixes and base blends described herein further comprise additives such as set retarding agents and set accelerating agents. Suitable set retarding agents include but are not limited to refined lignosulfonates. Suitable set accelerating agents include but are not limited to sodium sulfate, sodium carbonate, calcium sulfate, calcium carbonate, potassium sulfate, and potassium carbonate. Still other additives suitable for use in cement compositions comprising proportioned fluid loss additives as described herein include but are not limited to density modifying materials (e.g., silica flour, sodium silicate, microfine sand, iron oxides and manganese oxides), dispersing agents, strength retrogression control agents and viscosifying agents.

**[0017]** Water in the cement compositions according to the present embodiments is present in an amount sufficient to make a slurry of the desired density from the cement mix, and that is pumpable for introduction down hole. The water used to form a slurry can be any type of water, including fresh water, unsaturated salt solution, including brines and seawater, and saturated salt solution. According to some examples, the water is present in the cement composition in an amount of about 22% to about 200% by weight of the base blend of a cement mix. According to other examples, the water is present in the cement composition in an amount of from about 40%

to about 180% by weight of the base blend of a cement mix. According to still other examples, the water is present in the cement composition in an amount of from about 90% to about 160% by weight of the base blend of a cement mix.

**[0018]** The following examples are illustrative of the methods and compositions discussed above.

### EXAMPLE 1

**[0019]** The following describes exemplary cement compositions comprising proportioned fluid loss control additives as described herein, and the efficacy of such proportioned fluid loss control additives in such compositions.

**[0020]** Nine cement compositions (Nos. 1 - 9) comprising proportioned fluid loss control additives were prepared from the ingredients described in **Table 1A**.

**TABLE 1A**

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
<b>Base Blend</b>									
Cement (wt %)	60	60	60	60	60	60	60	60	60
Zeolite (wt %)	40	40	40	40	40	40	40	40	40
<b>Additive</b>									
Na <sub>2</sub> CO <sub>3</sub> (% bwob)	2.2	0	0	2.2	0	0	2.2	0	0
Na <sub>2</sub> SO <sub>4</sub> (% bwob)	4.4	0	0	4.4	0	0	4.4	0	0
HR-5 (% bwob)	0	0	1	0	0	1	0	0	0
Carbitron 20 (% bwob)	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
FWCA (% bwob)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
<b>Mixing Fluid</b>									
Water (% bwob)	94.59	94.59	94.59	126.53	126.53	126.53	150.45	150.45	150.45
D-Air 3000L (l/sk)	0.328	0.328	0.328	0.328	0.328	0.328	0.328	0.328	0.328
<b>Density (kg/m<sub>3</sub>)</b>	1500	1500	1500	1400	1400	1400	1350	1350	1350

**[0021]** Cement composition Nos. 1 – 9 were prepared according to procedures described in API Specification RP10B, 22<sup>nd</sup> edition, 1997, of the American Petroleum Institute, the entire disclosure of which is incorporated herein by reference. Generally, the procedure involved preparing a base blend by dry-mixing a cementitious material and zeolite by hand in a glass jar.

**[0022]** The amount of zeolite and cement comprising the base blend is as described in Table 1A, where “wt %” indicates the weight percent contributed to the total weight of the base blend. The cementitious material used in each base blend was Class C. Clinoptilolite, which is commercially available from C2C Zeolite Corporation of Calgary, Canada, was used as the zeolite in each base blend.

**[0023]** Sodium carbonate and sodium sulfate, in the amounts listed in Table 1A, where “% bwob” indicates a percentage based on the total weight of the base blend, were dry-mixed into the base blends of those compositions that were to undergo fluid loss testing at temperatures equal to or less than about 30° C (i.e., Nos. 1, 4 and 7) to accelerate the set of the cement at such temperatures.

**[0024]** HR-5, which is the tradename for a retarder comprising a refined lignosulfonate commercially available from Halliburton Energy Services, was dry-mixed into the base blends of cement composition Nos. 3 and 6 in the amount (% bwob) listed in Table 1A. The retarder served to slow the set time that would otherwise occur at the conditions (density and fluid loss test temperature) of the compositions.

**[0025]** Proportioned fluid loss additives (FLAs) were also dry-mixed into the base blends used for cement composition Nos. 1 – 9. In the examples illustrated in Table 1A, the proportioned fluid loss additives were Carbitron 20 and FWCA, which were dry-mixed into the base blend in the amounts (% bwob) as listed in Table 1A. Carbitron 20 is an unmodified non-hydrophobic hydroxyethylcellulose (HEC) having a molecular weight of about 225,000 atomic mass units, (amu), and is commercially available from Dow Chemical. FWCA is an unmodified non-hydrophobic hydroxyethylcellulose (HEC) having a molecular weight of about 1,000,000 amu, and is commercially available from Halliburton Energy Services.



[0026] The respective cement-zeolite base blends, and any accelerating additives, retarders, and proportioned fluid loss additives, comprised cement mixes from which cement composition Nos. 1 – 9 were formed.

[0027] Each cement composition was formed by adding the cement mix to a mixing fluid being maintained in a Waring blender at 4000 RPM. The cement mix was added to the mixing fluid over a 15 second period. When all of the cement mix was added to the mixing fluid, a cover was placed on the blender and mixing was continued at about 12,000 RPM for about 35 seconds. For each cement composition, the mixing fluid included water in the amounts as indicated in Table 1A. In certain compositions, the mixing fluid also included D-Air 3000L as reported in Table 1A. The amount of water is reported in Table 1A as a % bwob, and the amount of D-Air 3000L is reported in “l/sk”, which indicates liters of D-Air 3000L per sack of cement composition. D-Air 3000L is the tradename for a defoaming agent comprising polypropylene glycol, particulate hydrophobic silica and a liquid diluent, which is commercially available from Halliburton Energy Services, Duncan, Oklahoma. The cement mix temperature and mixing fluid temperature were both 24°C (75°F).

[0028] Cement composition Nos. 1 – 9 illustrate cement compositions comprising proportioned fluid loss additives (FLAs). The proportionality of the FLAs can be expressed as a ratio of the amounts of each FLA, where each amount is expressed as a weight percent of the total weight of the base blend (% bwob). Thus, in this Example 1, the proportionality of the FLAs, expressed as a ratio of the amounts (% bwob) of each type of FLA, can be described by a ratio of about 15:85, of a high molecular weight FLA to a low molecular weight FLA. In other examples, the amount of low molecular weight FLAs present in the base can be increased or decreased, with a complementary increase or decrease in the amount of high molecular weight FLAs. According to one such example, the amount of low molecular weight FLAs in the base blend decreases to about 0.75 % bwob, and the amount of high molecular weight FLAs increases to about 0.25 % bwob. In such an example, the proportionality of the FLAs can be described by a ratio of about 25:75 of high molecular weight FLAs to low molecular weight FLAs.

[0029] The proportionality of the FLAs can also be expressed as a ratio of the amount of high molecular weight FLA(s) to the amount of low molecular weight FLA(s), irrespective of the

amount each type contributes to the base blend. Thus, in this Example 1, the proportionality of the FLAs can be described as a ratio of about 1:5.67, meaning that the amount of low molecular weight FLAs present in the base blend is about 5.67 times the amount of high molecular weight FLAs present in the base blend. According to an example where the amount of low molecular weight FLAs present in the base blend has been decreased, such as to the 0.75 % bwob described above, and the amount of high molecular weight FLAs has been increased, such as to 0.25 % bwob described above, the proportionality of the FLAs can be described by a ratio of about 1:3 of high molecular weight FLAs to low molecular weight FLAs.

[0030] Yet another way to express the proportionality of the FLAs is in terms of their molecular weights. Thus, in this Example 1, where the high molecular weight FLA comprises an unmodified non-hydrophobic hydroxyethylcellulose (HEC) having a molecular weight of about 1,000,000 atomic mass units (amu) and the low molecular weight FLA comprises an unmodified non-hydrophobic HEC having a molecular weight of about 225,000 amu, the proportionality of the FLAs can be described as a ratio of about 4:1, meaning that the molecular weight of the high molecular weight FLA(s) present in the base blend is about 4 times the molecular weight of the low molecular weight FLA(s) in the base blend. In other examples, the molecular weight of the low molecular weight FLAs can be in the range of from about 100,000 amu to about 300,000 amu, while the molecular weight of the high molecular weight FLA can be in the range or from about 800,000 amu to about 1,200,000 amu. Thus, according to an example where the high molecular weight FLA has a molecular weight of about 1,200,000 amu and the low molecular weight FLA about 100,000 amu, the proportionality of the FLAs can be described by a ratio of about 12:1, meaning that the molecular weight of the high molecular weight FLA is about 12 times the molecular weight of the low molecular weight FLA. In an example where the high molecular weight FLA has a molecular weight of about 800,000 amu and the low molecular weight FLA has a molecular weight of about 300,000 amu, the proportionality of the FLAs can be described by a ratio of about 2.66:1, meaning that the molecular weight of the high molecular weight is about 2.66 times the molecular weight of the low molecular weight FLA.

[0031] Referring now to Table 1B, rheological data and fluid loss measurements of cement composition Nos. 1 – 9 are reported.

**TABLE 1B**

No.	Rheological Data									API Fluid Loss Test Temperature ° C (°F)	API Fluid Loss (mL/30 min)
	Temp. (°C)	Dial Readings (cp)									
		600 rpm	300 rpm	200 rpm	100 rpm	60 rpm	30 rpm	6 rpm	3 rpm		
1	30	n/a	196	145	89	65	47	34	32	30 (86)	84
2	50	245	175	131	84	62	43	21	18	50 (122)	76
3	80	99	60	39	22	15	10	7	6	80 (176)	100
4	30	157	101	75	47	34	25	19	18	30 (86)	134
5	50	105	66	48	28	19	12	5	4	50 (122)	150
6	80	57	38	23	12	7	5	4	2	80 (176)	176
7	30	108	65	46	26	21	15	10	8	30 (86)	227
8	50	57	36	25	15	10	6	1	0.5	50 (122)	243
9	80	54	36	30	25	17	11	8	7	80 (176)	364

**[0032]** The rheological data was determined using a Fann Model 35 viscometer. The viscosity was taken as the measurement of the dial reading on the Fann Model 35 at the different rotational speeds as indicated in 600 to 3 RPM, and at the temperatures as indicated in Table 1B. There are a number of theoretical models known to those of ordinary skill in the art that can be used to convert the values from the dial readings at the different RPM's into viscosity (centipoises). In addition, different viscometer models use different RPM values, thus, in some instances, a measurement is not available at a particular RPM value.

**[0033]** The rheological data was determined according to the procedures set forth in Section 12 of the API Specification RP 10B, 22nd Edition, 1997, of the American Petroleum Institute (the entire disclosure of which is hereby incorporated as if reproduced in its entirety). The foregoing API procedure was modified in that the initial reading at 300 RPM was taken after 60 seconds continuous rotation at that speed. Dial readings at 200, 100, 60, 30, 6 and 3 were then recorded in descending order at 20-second intervals. The final reading at 600 RPM was taken after 60 seconds continuous rotation at that speed.

**[0034]** The fluid loss testing was conducted according to procedures set forth in Section 10 of API Recommended Practice 10B, 22<sup>nd</sup> Edition, 1997, of the American Petroleum Institute (the entire disclosure of which is hereby incorporated as if reproduced in its entirety).

**[0035]** The procedures followed were those for testing at temperatures less than 194°F, with atmospheric pressure conditioning, and a static fluid loss cell. Generally, however, 475 cc of

each composition was placed into the container of an atmospheric pressure consistometer commercially available from Howco. The temperatures of the compositions were adjusted to the test temperatures indicated in Table 1B, (30, 50 and 80°C). The test temperatures were arbitrarily chosen, based on values that are often encountered as bottom hole circulating temperatures (BHCTs) of a variety of types of wells.

**[0036]** After about 20 minutes, the composition to be tested was stirred, and a 5 inch standard fluid loss cell, which was prepared according to the aforementioned Section 10 of API Recommended Practice 10B, was filled. The test was started within 30 seconds of closing the cell by application of nitrogen applied through the top valve. Filtrate was collected and the volume and time were recorded if blow out occurred in less than 30 minutes or volume recorded at 30 minutes if no blow out occurred. Thus, to determine the fluid loss data reported in Table 1B, values were calculated as twice the volume of filtrate multiplied by 5.477 and divided by the square root of time if blowout occurred, and as twice the volume of filtrate if blowout did not occur within 30 minutes.

**[0037]** The measured fluid loss values (mL of fluid lost/30 min) of cement composition Nos. 1 – 9 illustrate that proportioned fluid loss additives provide effective fluid loss control to cement compositions having a variety of densities, and at temperatures at least up to 80°C (176°F). In addition, the rheological data of cement composition Nos. 1 – 9 is within acceptable parameters.

**[0038]** Although only a few exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many other modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention as defined in the following claims.